

REPORT ON THE GRAVIMETRIC MICRODETERMINATION OF SULFUR

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The previous studies of the determination of sulfur¹ produced a volumetric method which was suitable as an official procedure, but the gravimetric method tested did not give sufficiently good between-laboratory precision to warrant recommending it as an A.O.A.C. method. A gravimetric method is required because sulfur should not be determined by the volumetric procedure if the material being analyzed contains phosphorus. Consequently a revised gravimetric procedure was subjected to a collaborative test in which the same two pure samples (benzyl-isothiurea hydrochloride and sulfanilamide) were employed that had been used in the two previous studies. The new tentative method described

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¹ Ogg, C. L., *This Journal*, 35, 305 (1952); 36, 335 (1953).

below was designed to test the need for a double washing and ignition of the precipitated barium sulfate. It had been assumed that such a procedure was unnecessary because in the present A.O.A.C. micromethods for sulfur the solutions from which the sulfate would be precipitated contain only small amounts of foreign ions which might be adsorbed or coprecipitated with the barium sulfate. To test this assumption and to try to find a suitable method, a copy of the following tentative gravimetric procedure was sent to each collaborator. Each analyst was asked to use either the Carius or the catalytic combustion methods (both first action) to convert the sulfur to sulfate and then to determine the sulfate by the tentative procedure.

GRAVIMETRIC PROCEDURE FOR CARIUS COMBUSTION METHOD

Dissolve residue in 3 ml distd H_2O , pour into previously ignited and weighed porcelain crucible, rinse beaker with four 2 ml portions H_2O , and place crucible on steam bath until soln is near boiling point. (If total vol. exceeds 10–11 ml, evap. to this vol.) Add, dropwise, 0.5 ml 10% $BaCl_2$ (for samples which might contain more than 5 mg S, use 1 ml), digest at least 15 min., and cool 15 min. Connect porcelain filter, previously ignited and weighed with crucible, to arm of siphon with rubber tubing; connect other arm of siphon to suction flask thru a rubber stopper. Lower filter into crucible; draw off soln slowly; rinse ppt, walls of crucible, and filter with three 3 ml portions 1:300 HCl , drawing off as much liquid as possible. Carefully detach filter, place in crucible, wipe outside of crucible and end of filter with moist chamois or cheesecloth, and handle thereafter with crucible tongs. Place crucible and filter in larger crucible and dry in oven at ca $110^\circ C$. for 10 min. Then ignite in muffle at $700\text{--}750^\circ C$. for 10 min. (ppt may be ignited by heating larger crucible contg crucible and stick to dull red heat with Meker burner), cool on metal block for 30 min. (or in desiccator for 1 hr), and weigh. Make blank run on reagents. Repeat treatment of ppt beginning, "rinse ppt, walls of crucible . . ."

Calculation: $(wt\ BaSO_4 - blank) \times 0.1374 \times 100 / \text{sample wt} = \% S$.

GRAVIMETRIC PROCEDURE FOR CATALYTIC COMBUSTION METHOD

Rinse contents of absorber quantitatively into previously ignited and weighed porcelain crucible, using five 2 ml portions H_2O . Continue as under Carius method, beginning " . . . place crucible on steam bath . . ."

RESULTS

Five collaborators reported 52 and 46 values for samples 1 and 2, respectively. These data are summarized in Table 1, where n is the number of values reported, \bar{x} is the mean, and s is the standard deviation of the collaborator's individual values; $\bar{\bar{x}}$ is the mean and $s_{\bar{x}}$ is the standard deviation of the mean (\bar{x}) values.

Examination of the data shows that the single ignition treatment of the $BaSO_4$ from sample 1 gave the more accurate value, 15.85 versus the theoretical value of 15.82, whereas the value by double ignition was 15.63, or 0.19 per cent low.

The t value, 2.64, calculated for the difference between means exceeded the critical $t_{0.05}$ (2.37). The two treatments, therefore, produced significantly different means. The introduction of a constant error by this

TABLE 1.—*Results of sulfur determination by tentative micromethod
(effect of single and double ignition)*

COLLABORATOR NO.	SINGLE IGNITION ^a			DOUBLE IGNITION ^b		
	<i>n</i>	\bar{x}	<i>s</i>	<i>n</i>	\bar{x}	<i>s</i>
Sample 1: Benzylisothiurea hydrochloride (15.82% S)						
9	4	15.70	0.15			
15	8	15.71	0.12	8	15.62	0.09
29	8	15.90	0.11	8	15.47	0.19
40	4	15.97	0.07	4	15.70	0.06
59	4	15.96	0.14	4	15.71	0.05
\bar{x}		15.85	(0.12)		15.63	(0.10)
$s_{\bar{x}}$		0.13			0.11	
Sample 2: Sulfanilamide (18.62% S)						
9	6	18.69	0.14			
15	8	18.51	0.30	8	18.42	0.25
29	4	18.84	0.01	4	18.78	0.05
40	4	18.86	0.12	4	18.63	0.13
59	4	18.93	0.14	4	18.47	0.05
\bar{x}		18.77	(0.14)		18.58	(0.13)
$s_{\bar{x}}$		0.17			0.16	

^a BaSO₄ washed and ignited once.

^b BaSO₄ from single treatment rewashed and reignited.

treatment is indicated by the fact that the theoretical value falls outside the 95 per cent confidence limits for the mean of the data from the double ignition.

The data for sample 2 show that the double ignition again lowered the values by the same amount, but in this case the mean for the single ignition is considerably higher and that for the double ignition only a little lower than the theoretical value. The *t* value of 1.71, however, did not exceed the critical *t*_{0.05} (2.37), showing that the difference between means for sample 2 was not significant.

The theoretical value also was bracketed by the confidence limits of the mean for the single ignition data.

From these findings, it is concluded that the single ignition treatment following the proposed procedures is the better. The within-laboratory precision (*s* values) was generally good; the between-laboratory precision, (*s*_{*x*} values of 0.13 and 0.17 per cent for samples 1 and 2, respectively) seems quite satisfactory; and the agreement between the over-all mean (\bar{x}) and the theoretical value is good for sample 1 (0.03 per cent) and acceptable for sample 2 (0.15 per cent).

There is evidence that values from the single ignition procedure tend to be high. To try to bring these values closer to the theoretical value, collaborator 59 proposed that the precipitated barium sulfate be washed 5 or 6 times with 1:300 hydrochloric acid instead of the 3 times specified in the method and, of course, that the double ignition be eliminated. Whether or not this will have a significant effect on the results is not certain, but such a change should not decrease the accuracy of the results. The Referee proposes that the procedure be changed accordingly.

RECOMMENDATIONS

It is recommended†—

(1) That the gravimetric method tested this year be changed as follows:

- (a) Change sentence 8, above, from "...rinse... with three 3 ml portions 1:300 HCl..." to "...rinse... with five or six 3 ml portions 1:300 HCl..."
- (b) Delete last sentence: "Repeat treatment of ppt beginning, 'rinse ppt, wall of crucible...'"

(2) That the amended procedure be adopted as first action.

COLLABORATORS

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† For report of Subcommittee C and action of the Association, see *This Journal*, 38, 77 (1955).